

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN POLYPHENYLENE ETHER COMPOSITIONS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to improvements in polyphenylene ether compositions and in particular to impact resistant polyphenylene ether resins having improved mold flow properties. More particularly, it pertains to compositions comprising a polyphenylene ether resin, a styrene resin and an impact improver combination (i) an A—B—A¹ type block copolymer and (ii) a hydrogenated derivative of (i).

The compositions provide molded articles of good impact strength and superior flow in the mold.

The polyphenylene ether resins are described by way of illustration, in Hay, U.S. 3,306,874 and 3,306,875 and in Stamatoff, U.S. 3,257,357 and 3,257,358.

In the Hay patents, polyphenylene ether resins are prepared by an oxidative coupling method comprising passing an oxygen-containing gas through a reaction solution of a phenol and a metal-amine complex catalyst. In the Stamatoff patents, polyphenylene ethers are prepared by reacting the corresponding phenolate ion with an initiator, i.e., an acid peroxide, in the presence of a complexing agent.

It has been proposed that compositions of polyphenylene ether resin and polystyrene can be modified by the inclusion of block copolymers of the vinyl aromatic compound, i.e., styrene, and a conjugated diene, e.g., butadiene. Such compositions, which have excellent impact resistance, are disclosed in U.S. Patent 3,994,856. Compositions of a polyphenylene ether resin, a styrene resin and a block copolymer of an aromatic hydrocarbon such as styrene and a conjugated diene such as butadiene which has had its unsaturation reduced to less than 10% of its original value have also been proposed. These are disclosed in British Patent 1,477,706.

It has now been discovered, quite unexpectedly, that using a combination of a block copolymer of the unsaturated type and a block copolymer of the saturated type will provide impact strengths better than using either one separately. This discovery permits important cost reductions in the hydrogenated block copolymer-based systems and improvement in melt flow in the unsaturated block copolymer systems, either one with improved impact properties. The new compositions can be modified with conventional thermoplastic additives, such as pigments, other flame-retardants, anti-oxidants, plasticizers, fillers and reinforcing glass fibers.

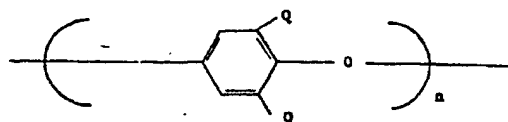
According to this invention, there are provided thermoplastic compositions useful for molding, e.g., injection molding, compression molding, transfer molding, and the like, which possess good impact resistance after molding, the compositions comprising:

- (a) a polyphenylene ether resin,
- (b) a styrene resin, and
- (c) an impact improver combination

comprising (i) from 99 to 1 parts by weight of an elastomeric block copolymer of the

A—B—A' type, wherein terminal blocks A and A' are the same or different and are polymerized vinyl aromatic hydrocarbons and center block B is a polymerized conjugated diene, the molecular weight of B being higher than the combined molecular weights of A and A', and (ii) from 99 to 1 parts by weight of a hydrogenated derivative of component (i).

The polyphenylene ether resin is preferably one which is comprised of the formula:



wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is hydrogen or a monovalent substituent selected from halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and phenyl nucleus.

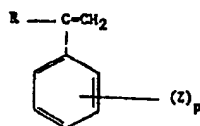
For purposes of the present invention, an especially preferred family of polyphenylene ethers include those having alkyl substitution in the two positions ortho to the oxygen ether atom, i.e., those of the formula wherein each Q is alkyl, most preferably having from 1 to 4 carbon atoms.

The most preferred polyphenylene ether resin for the purposes of this invention is poly(2,6-dimethyl-1,4-phenylene) ether.

In general, the polyphenylene ether resins of this invention can be prepared by following procedures fully described in the abovementioned patents of Hay and Stamatoff. The polyphenylene ethers are self-condensation products of monohydric monocyclic phenols typically produced by reacting the phenols in the presence of a complexing agent or complex metal, e.g., copper catalyst. In general, the molecular weight will be controlled by the reaction time, longer times providing a higher average number of repeating structural units. Termination can be brought about by the use of conventional means. For instance, in the case of reaction systems which make use of complex metal catalysts, the polymerization reaction can be terminated by adding an acid, e.g., hydrochloric or sulfuric acid, or the like, or a base, e.g., lime, sodium hydroxide, potassium hydroxide, and the like, or the product is separated from the catalyst by filtration, precipitation or other suitable means, as taught by Hay in U.S. 3,306,875.

After the product is precipitated and recovered, it may be redissolved and reprecipitated, as desired, to remove impurities. Finally, it is filtered, washed and dried.

The styrene resins (b) are described in detail in Cizek, U.S. 3,383,435. In general, they will have at least 25% by weight of polymer units derived from a vinyl aromatic compound of the formula:



wherein R is hydrogen, (lower) alkyl or halogen, Z is vinyl, halogen or (lower) alkyl; and p is 0 or an integer of from 1 to the number of replaceable hydrogen atoms on the benzene nucleus. Herein, the term "(lower)alkyl" is intended to mean alkyl of from 1 to 6 carbon atoms.

Included among these are homopolymers such as polystyrene and monochloropolystyrene, as well as modified styrene resins, such as rubber-modified high-impact polystyrene, and the styrene containing copolymers such as the styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers, styrene-acrylonitrile- α -alkyl styrene copolymers, styrene-acrylonitrile-butadiene copolymers (ABS), poly- α -methylstyrene, copolymers of ethylvinylbenzene and divinyl benzene, copolymers of styrene and maleic anhydride.

The elastomeric block copolymers (c) (i) and (c) (ii) are of the A—B—A¹ type in which the center and terminal block vary. In the compositions of this invention, the center block, B, is derived from a conjugated diene, e.g., butadiene, isoprene; 1,3-pentadiene or 2,3-dimethyl butadiene, and terminal blocks A and A¹ are derived from a vinyl aromatic compound, e.g., styrene, α -methyl styrene, vinyl toluene, vinyl naphthalene, or the like. In the most preferred compositions, the block copolymer will have terminal blocks A and A¹ comprised of polystyrene and center block B comprised of polybutadiene or polyisoprene.

The ratios of the comonomers can vary broadly, so long as the molecular weight of the center block is greater than the combined molecular weights of the terminal blocks. Preferably, within this limitation, the molecular weight of the terminal block will range from 2,000 to 150,000 and that of the center block will range from 25,000 to 1,000,000.

With respect to component (c) (i), such copolymers can be prepared by an organometallic initiation process using, for example, sodium or lithium metal or an organic derivative thereof. The diene monomers can be polymerized with a monofunctional or difunctional initiator, as is described in detail in "Polymer Chemistry of Synthetic Elastomers", edited by Kennedy et al, Interscience Publishers, Vol. 23, Part II (1969), pages 553—559, incorporated herein by reference.

Other methods of preparation are described in Zelinski, U.S. 3,251,905 and Holden et al, U.S. 3,231,635.

With respect to component (c) (ii), these will be hydrogenated A—B—A¹ block copolymers, especially block copolymers, of the above type wherein the average unsaturation of the center block, B, has been reduced to less than 20% of its original value.

In the case of the hydrogenated block copolymers, it is preferred to form terminal blocks A and A¹ having an average molecular weight of from 4,000 to 115,000 and center block B with an average molecular weight of from 20,000 to 450,000.

The hydrogenated block copolymers usually confer better thermal stability and flow properties, e.g., melt viscosity, at elevated temperatures than the unhydrogenated block copolymers.

Hydrogenation may be conducted using a variety of hydrogenation catalysts, e.g., nickel, Raney nickel, copper chromate, molybdenum sulfide and finely divided platinum, on a low surface area carrier. The hydrogenation can be carried out at any desired temperature or pressure, from atmospheric to 3,000 p.s.i.g., the usual range being between 100 and 1,000 p.s.i.g., at temperatures of from 75 to 600° F., for a period of time ranging from 0.1 to 24 hours, preferably 0.2 to 8 hours.

The preparation of the hydrogenated block copolymers is described in detail in Jones, U.S. 3,431,323.

As is taught in Cizek, U.S. Patent 3,383,435, the polyphenylene ethers and styrene resins are combinable in all proportions, e.g., from 1 to 99 parts of polyphenylene ether resin and from 99 to 1 parts of styrene resin. Similarly, the relative amount of A—B—A¹ block copolymers (e) (i) and (c) (ii) in the compositions of this invention can vary broadly. Preferred compositions will comprise from 10 to 90 parts by weight of polyphenylene ether resin (a), from 90 to 10 parts by weight of styrene resin (b) and from 0.5 to 20 parts by weight of A—B—A¹ block copolymer (c) (i) and from 0.5 to 20 parts by weight of hydrogenated A—B—A¹ block copolymer, based on 100 parts by weight of the resins component of the composition.

Other ingredients can also be included in the compositions of this invention, e.g., pigments, dyes, flame retardants, drip retardants, plasticizers, antioxidants, reinforcing agents and fillers.

A reinforcing agent comprised of fibrous glass is preferred. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. The preferred filaments for plastics reinforcement are made by mechanical pulling. The filament diameters range from 0.00012 to 0.00075 inch, but this is not critical to the present invention.

The length of the glass filaments and whether or not they are bundled into fibers and the fibers bundled in turn to yarns, ropes or rovings, or woven into mats, and the like, are also not critical to the invention. However, in preparing the molding compositions, it is convenient to use the filamentous glass in the form of chopped strands of from one-eighth to 2 inches long. In articles molded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable, however, because the best properties are exhibited by thermoplastic injection molded articles in which the filament lengths lie between 0.000005 and 0.125 (one-eighth) inch.

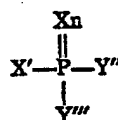
In general, best properties will be obtained if the sized filamentous glass reinforcement comprises from at least 1 to about 80% by weight, based on 100 parts by weight of resin.

In applications where self-extinguishing compositions are required, flame retardant agents may be included. Illustrative flame retardant additives are disclosed in U.S. 3,833,685, U.S. 3,341,154, U.S. 3,915,926 and U.S. 3,671,487.

Other flame retardants are disclosed in U.S. 3,681,281, and U.S. 3,557,053, U.S. 3,830,771 and U.K. 1,358,080.

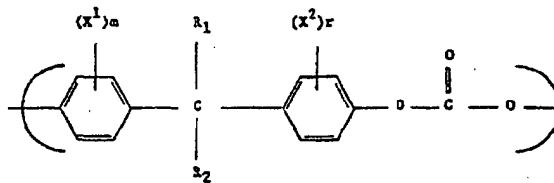
In general, the preferred flame retardants are phosphorus compounds. These are selected from elemental phosphorus or organic phosphonic acids, phosphonates, phosphinates, phosphonites, phosphinites, phosphene oxides, phosphenes, phosphites or phosphates. Illustrative are triphenyl phosphine oxide. This can be used alone or mixed with hexabromobenzene or a chlorinated bisphenyl and, optionally, antimony oxide.

Typical of the preferred phosphorus compounds to be employed in this invention would be those having the general formula:



in which $X=S$ or O , and $n=0$ or 1 , Y' , Y'' and Y''' are the same or different and represent alkyl, halocycloalkyl, halocycloalkyl aryl, alkyl substituted aryl, halogen substituted aryl, aryl substituted alkyl, alkyloxy, cycloalkyloxy, halogen substituted alkyloxy, aryloxy, halogen substituted aryloxy, or halogen. Two of the Y 's may be combined into a cyclic structure, or one or two of the Y 's may be difunctional in which case the compounds consists of short or long chain compounds containing a plurality of P atoms per molecule. Typical examples of suitable phosphorus compounds include: triphenyl phosphate, diphenyl phenyl phosphonate, phenyl diphenyl phosphinate, triphenyl phosphine, triphenyl phosphine oxide, tris (p-bromophenyl) phosphate, neopentyl phenyl phosphonate, tris (dibromopropyl) phosphate, dibenzyl phenyl phosphonate, poly (1,4 cyclo hexylene dimethylene) phenyl phosphonate and pentaerythritol bis(p bromophenyl) phosphonate. A preferred flame retardant is a tris(polyhalophenyl) phosphate, e.g., tris(tri-bromophenyl) phosphate.

Special mention is made of flame retardant additives consisting of aromatic carbonate homopolymers having repeating units of the formula:



wherein R^1 and R^2 are hydrogen, (lower)alkyl or phenyl, X^1 and X^2 are bromo or chloro and m and r are from 1 to 4. These materials may be prepared by techniques well known to those skilled in the art. Also preferred are aromatic carbonate copolymers in which from 25 to 75 weight percent of the repeating units comprise chloro- or bromo-substituted dihydric phenol, glycol or dicarboxylic acid units. See, e.g., A.D. Wambach, U.S. 3,915,926, Procedure A.

The amount of flame retardant additive, if used, is not critical to the invention, so long as it is present in a minor proportion based on said composition—major proportions will detract from physical properties—but at least sufficient to render the polyphenylene ether-based resin fire resistant or self-extinguishing. Those skilled in the art are well aware that the amount will vary with the nature of the resin and with the efficiency of the additive. In general, however, the amount of additive will be from 0.5 to 40 parts by weight per 100 parts of resin.

The compositions of this invention can be prepared by blending the components to form a premix, passing the latter through an extruder at an elevated temperature, e.g., 425° to 640° C., cooling and chopping the extrudate into pellets, and molding them into the desired shape.

5 The following examples illustrate the compositions of the invention. They are set forth merely as a further illustration and are not to be construed as limiting the invention in any manner. 5

EXAMPLES 1—6.

10 Compositions of poly(2,4-dimethyl-1,4-phenylene ether) resin, intrinsic viscosity about 0.48 deciliters/gram as measured in chloroform at 30° C., a styrene resin (Solar gp ("crystal" grade homopolystyrene, number average molecular weight about 62,000), the styrene-butadiene-styrene block copolymers (as shown in Table 1), tri-
15 decyl phosphite, zinc sulfide, zinc oxide and titanium dioxide are prepared by extrusion at 575° F., chopped and molded in an injection molding machine.* The formulations and physical properties are summarized in Table 1. 15

* At 500° F. (Cylinder) and 190° F. (mold).

TABLE 1

Compositions of poly(2,6-dimethyl-1,4-phenylene ether), homopolystyrene and styrene-butadiene-styrene block copolymer

Example	1*	2*	3	4*	5*	6
<u>Ingredients (parts by weight)</u>						
poly(2,6-dimethyl-1,4-phenylene ether)	30	30	30	30	30	30
polystyrene	50	50	50	40	40	40
unhydrogenated styrene butadiene styrene block copolymer ^a	20	—	10	30	—	15
hydrogenated styrene-butadiene-styrene block copolymer ^b	—	20	10	—	30	15
tridecyl phosphite	1.0	1.0	1.0	1.0	1.0	1.0
zinc sulfide	0.15	0.15	0.15	0.15	0.15	0.15
zinc oxide	0.15	0.15	0.15	0.15	0.15	0.15
titanium dioxide	3.0	3.0	3.0	3.0	3.0	3.0

* Control Experiment.

^a K 1101, Shell Chem. Co., Polymers Division.^b Kraton G 6521, Shell Chem. Co., Polymers Division.

TABLE 1 (Continued)

Physical Properties

Example	1*	2*	3	4*	5*	6
<u>Properties</u>						
Tensile yield, psi	7.7	8.0	7.4	6.4	5.9	5.7
Tensile strength, psi	6.6	6.6	6.5	6.4	5.8	5.6
Tensile elongation, %	50	20	29	55	33	36
Izod impact, ft. lbs./in.n.	4.2	2.3	4.9	5.3	5.8	7.0
Gardner impact, in. lbs. 73°F.	195	205	235	260	170	195
-40°F.	95	10	200	190	270	255
Heat Distortion Temp., °F.	239	243	241	241	237	242
Flow channel length, in.	19	29.75	25	13.5	27	21.5

* Control Experiment.

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EXAMPLES 7-9.

5 Using the procedure described in Examples 1-6, blends of poly(2,6-dimethyl-1,4-phenylene ether) resin, intrinsic viscosity about 0.48 deciliters/gram as measured in chloroform at 30° C., a styrene resin (KPTL-5, ARCO Chemical Co., a "crystal" grade homopolystyrene, number average molecular weight 41,600), the styrene-butadiene-styrene block copolymers (as shown in Table 2), tridecyl phosphite, zinc sulfide and zinc oxide are prepared. The formulations and properties are summarized in Table 2.

5

TABLE 2

Compositions of poly(2,6-dimethyl-1,4-phenylene ether) homopolystyrene and styrenebutadiene-styrene block copolymer

Example	7*	8*	9
Ingredients (parts by weight)			
poly(2,6-dimethyl-1,4-phenylene ether)	70	70	70
polystyrene	30	30	30
unhydrogenated styrene-butadiene-styrene block copolymer ^a	10	—	5
hydrogenated styrene-butadiene-styrene block copolymer ^b	—	10	5
tridecyl phosphite	0.5	0.5	0.5
zinc sulfide	0.15	0.15	0.15
zinc oxide	0.15	0.15	0.15

* Control Experiments.

a as in Examples 1-6.

b as in Examples 1-6.

TABLE 2 (Continued)

Example	7*	8*	9
Properties			
Tensile yield, psi	12.4	10.5	11.5
Tensile strength, psi	10.5	8.8	9.4
Tensile elongation, %	67	52	68
Izod impact, ft. lbs./in. n.	0.9	2.7	2.1
Gardner impact, in lbs. 73°F.	50	210	280
Heat Distortion Temp., °F.	292	299	290
Flow channel length, in.	16	25.75	20.25

* Control Experiment.

As can be seen, the combination of impact modifiers permits less of the more expensive hydrogenated block copolymer to be used, and furthermore, the melt flow of the unhydrogenated block copolymer—containing compositions is improved to a degree greater than would be expected.

Having regard to the provisions of Section 9 of the Patents Act 1949, attention is directed to the claims of our co-pending British Patent Application No. 52901/77 (Serial No. 1,559,263) which relates to a thermoplastic composition comprising:

- (a) a low molecular weight polyphenylene ether resin, having an intrinsic viscosity of less than 0.4 deciliters/gram when measured in solution in chloroform at 30° C.;
- (b) a styrene resin, and
- (c) an elastomeric block copolymer of the A—B—A' type, wherein terminal blocks A and A' are the same or different and are polymerized vinyl aromatic hydrocarbons and center block B is a polymerized conjugated diene, the molecular weight of B being higher than the combined molecular weights of A and A'.

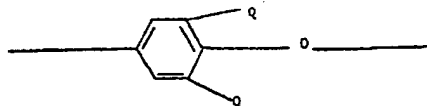
WHAT WE CLAIM IS:—

1. A thermoplastic composition comprising:

- (a) a polyphenylene ether resin;
- (b) a styrene resin, and

(c) an impact improver comprising (i) from 99 to 1 parts by weight of an elastomeric block copolymer of the A—B—A' type, wherein A and A' are polymerized vinyl aromatic hydrocarbon blocks and B is a polymerized conjugated diene, block the molecular weight of B being higher than the combined molecular weights of A and A', and (ii) from 99 to 1 parts by weight of a hydrogenated derivative of component (i).

2. A composition as defined in Claim 1 wherein said polyphenylene ether resin contains at least 50 structural units of the formula:



wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, and Q is hydrogen or a monovalent substituent selected from halogen, hydrocarbon radicals free of a tertiary alpha-carbon atoms, halohydrocarbon and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, and hydrocarbonoxy radicals.

3. A composition as claimed in claim 1 or claim 2 wherein said polyphenylene ether is poly(2,6-dimethyl-1,4-phenylene) ether.

4. A composition as claimed in any one of claims 1 to 3 wherein said styrene resin is a homopolystyrene resin.

5. A composition as claimed in any one of claims 1 to 3 wherein said styrene resin is a rubber modified high impact polystyrene resin.

6. A composition as claimed in any one of the preceding claims wherein in components (c) (i) and (c) (ii), each A and A' has an average molecular weight of 2,000 to 150,000 and B has an average molecular weight of 25,000 to 1,000,000.

7. A composition as claimed in any one of the preceding claims wherein in component (c) (ii), the average unsaturation B has been reduced to less than 20% of its original value.

8. A composition as claimed in any one of the preceding claims wherein in components (c) (i) and (c) (ii), each A and A' has an average molecular weight of 4,000 to 115,000 and B has an average molecular weight of 20,000 to 450,000.

9. A composition as claimed in any one of the preceding claims wherein A and A' are polymerized styrene, α -methyl styrene, vinyl toluene, vinyl xylene or vinyl naphthalene blocks, and B is a polymerized butadiene, isoprene, 1,3-pentadiene or 2,3-dimethylbutadiene block.

10. A composition as claimed in any one of the preceding claims which comprises by weight 10 to 90 parts of poly phenylene ether resin (a), 90 to 10 parts of styrene resin (b), 0.5 to 20 parts of A—B—A' block copolymer (c) (i) and 0.5 to 20 parts of hydrogenated A—B—A' block copolymer.

5 11. A composition as claimed in claim 1 substantially as hereinbefore described in any one of Examples 3, 6 or 9. 5

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